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Effect of Mechanical Compression and Hydrostatic Pressure on the Molecular Mobility of Poly(lactic acid)

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Summary: The molecular mobility of an organic glass (PLA with 4.3% of D-lactic acid content) was investigated by calculating the size of the Cooperative Rearranging Regions (CRR) at its glass transition. The samples were exposed to different external constraints – namely a large deformation by mechanical compression at $T < Tg$ (prior to measurement) or different hydrostatic pressures (during the measurement). The measurements were performed by Differential Scanning Calorimetry (DSC) techniques: standard, temperature modulated (TM-DSC) and high pressure (HP-DSC). It was shown that mechanical deformations above the elastic limit increase the CRR size and shift the Tg value to higher temperatures, but have no effect on the value of $\Delta Cp(Tg)$. On the other hand, increasing the hydrostatic pressure during the measurement (1 to 100 bar) decreases the CRR size, slightly influences Tg and does not change the value of $\Delta Cp(Tg)$.

Keywords: compression; CRR; molecular mobility; PLA; pressure

Introduction

During its life cycle, a polymer is likely to undergo several constraints which could modify its behavior, physical ageing and life time expectancy. Mechanical deformations probably represent the category of constraints that includes the most sever actions to which a polymer could eventually be exposed. Polymer processing, for instance, requires high shearing rates in the molten state and sometimes high draw ratios in the rubbery state ($T > Tg$). Both these actions tend to stretch the polymer chains in one direction and eventually compress the polymer fibers in the direction perpendicular to the mechanical load.[1,2] Mechanical deformations induced by shear, draw and compressive stresses in the molten and rubbery states are the leitmotif of polymer processing techniques such as extrusion, film blowing, injection molding, thermoforming, compression and transfer molding, and several papers dealing with the effects of the processing conditions on the final polymer properties are available in the literature.[3–10] However, some of the properties obtained right after processing can only be pretended to be final, as sometimes (as for the glass transition temperature,[11] the impact strength,[12] the barrier properties[9] and the water sorption,[13] for instance) they depend on the molecular mobility of the polymer chains, which evolves with time as the polymer glassy phase undergoes physical ageing.[14–16] It goes without saying that sometimes polymers are not allowed to undergo pure physical ageing during their life cycle, as they also have to resist mechanical stresses in the glassy state. The ability of a polymer to get deformed under a stress applied in the glassy or rubbery state is commonly evaluated by tensile creep tests.[17,18] It is rare, however, to have the results of tensile creep tests

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correlated to the molecular mobility. In addition, the literature it is easier to find works describing the effects of tensile (stretching) deformations on the molecular mobility[10,17,19–21] instead of those of a mechanical compression. It is worth pointing out that having a polymer mechanically compressed may not achieve the same effect as having it surrounded by a pressurized gas (hydrostatic pressure). Both conditions represent external actions to which a polymer could eventually get exposed during its life cycle, but the literature generally lacks of works dealing with either one of these aspects and their influence on the molecular mobility of the macromolecular chains.

Poly (lactic acid) (PLA) is probably the most popular biopolymer, as the number or works about it has unceasingly increased in the last few decades. Its popularity comes from its green side, as it is known to be bio-sourced, recyclable as any other thermoplastic, compostable and biodegradable when placed in a suitable environment.[22,23] Its monomer can be obtained by fermenting the glucose extracted from starch-rich plants (e.g. corn and beet); lactic acid oligomers are then formed by step-growth condensation. The following step is the ring-opening polymerization of the lactic acid oligomers. As the naturally occurring form of lactic acid is the L-isomer (i.e. the monomer spontaneously obtained through the fermentation of sugars is the L-lactic acid), PLLA is the most common form of green PLA. However, different ratios of L-lactic acid and D-lactic acid lead to polymers having different morphologies and properties. In general, the presence of D-lactic acid interferes with polymer crystallization, increasing the chances to get a substantially amorphous PLA. When it comes to studying molecular mobility, the target polymer should be mostly amorphous (rather than highly crystalline) as molecular mobility is determined through the glass transition of the amorphous phase.

The molecular mobility in an amorphous polymer can be inferred by calculating the average size of the Cooperative Rearranging Regions (CRR) involved in the glass transition. The CRR concept was originally introduced by Adam and Gibbs[24] and then developed and adapted to thermal characterization techniques by Donth.[25] A CRR is the formal representation of the smallest amorphous domain undergoing molecular relaxation at a given temperature. In other words, a CRR is a portion of material virtually composed of all the moieties (evenly distributed in the entire volume of the glassy phase) undergoing a conformational rearrangement characterized by the same relaxation dynamics. When a glass-forming liquid is cooled down till its glass transition, the molecular motions of its moieties progressively slow down. As the glass transition is reached, these molecular motions start to become cooperative, and CRR appear as soon as the molecular motions become cooperative. The size of a CRR (the so-called cooperative length) being temperature-dependent, it keeps on increasing as the temperature of the glass decreases. The CRR concept has been widely used to characterize the molecular mobility of glass-forming systems, both organic and inorganic.[10,19,26–29] According to Donth, the volume of a CRR at the dynamic glass transition temperature T_α can be calculated as

$$V_\alpha = \frac{\Delta(1/C_p)}{\rho(\delta T)^2} k_B T_\alpha^2 \quad (1)$$

where

$$\Delta(1/C_p) = (1/C_p)_{glass} - (1/C_p)_{liquid} \text{ at } T = T_\alpha \quad (2)$$

and ρ is the polymer density, $2\delta T$ is the full width at half maximum (FWHM) of the dynamic relaxation peak (C" signal recorded at the glass transition by TM-DSC or, in the absence of temperature modulation, the derivative of the normalized heat flow signal recorded at the glass transition by standard DSC), $k_B = 1.38 \cdot 10^{-23}$ J/K is the Boltzmann constant and T_α is the dynamic glass transition

temperature (corresponding to the maximum of the dynamic relaxation peak).

In this work, a PLA with a low content (4.3%) of D-lactic acid (thus essentially amorphous) was exposed to different external actions and characterized by Differential Scanning Calorimetry (DSC) techniques to point out the possible effects of such external factors on the molecular mobility evaluated through the calculation of the CRR size. The applied constraints were either a mechanical compression (up to 1.5 GPa) exerted at room temperature (i.e. in the glassy state) prior to measurement, or a series of hydrostatic pressures (0.1 to 10.0 ± 0.002 MPa) imposed in the calorimeter cell during the measurement while heating the sample through its glass transition.

Material and Methods

PLA 4042D was purchased from NatureWorks LLC. It is a polymer whose L-lactic acid monomers are extracted from corn and polymerized in the presence of 4.3% of D-lactic acid monomers. Its density is 1250 kg/m^3. The number-average molecular weight is 116000 g/mol and the weight-average molecular weight is 188000 g/mol (repeating unit 90 g/mol). The polymer pellets were used as received to prepare thick films, which were subsequently cut by a paper puncher as small discs perfectly fitting into standard DSC aluminum pans. Before applying any external constraint, the samples were rejuvenated *in situ* (i.e. in the cell of the calorimeter used for the subsequent thermal characterizations) by heating the polymer up to 180 °C. Standard DSC measurements on freshly rejuvenated (zero-ageing) PLA samples gave a reference (zero-constraint) glass transition temperature of about 58 °C (heating rate = cooling rate = 10 °C/min).

The mechanical compression of the freshly rejuvenated PLA samples was achieved by a hydraulic manual press (SPECAC 25T) having a maximum nominal force of 25 tons = $2.5 \cdot 10^5$ N (when applied to the surface of the DSC aluminum pan, this corresponds to a maximum uniaxial compressive stress of 1.5 GPa). The force was applied and maintained during 15 min at room temperature (i.e. on the polymer in its glassy state). As plastic deformation gradually occurred, the force was regularly adjusted at its maximum value until it stabilized. This external action corresponded to a mechanical compression of the PLA samples above their limit of elasticity, which was found to be equal to 120 MPa for PLA 4042D cylinders measuring 22 mm (L) × 11 mm (Ø), uniaxially compressed with a deformation rate of 1.3 mm/min as required by ASTM D695 standards (result not shown). The compressive stress induced an average permanent deformation of the samples of about 0.64 mm/mm. Right after mechanical compression, the flattened samples were hole-punched again to fit into a new aluminum pan.

Standard DSC measurements were then performed on a DSC Q100 calorimeter (TA Instruments, USA) under nitrogen flow (50 mL/min). Prior to measurement, both indium and zinc standards were used for energy and temperature calibrations. The polymer glass was formed with a cooling rate of 10 °C/min and the heating rate for the measuring ramp was also set at 10 °C/min.

Temperature Modulated DSC (TM-DSC) measurements were performed on the same DSC Q100 calorimeter under nitrogen flow (50 mL/min) after appropriate calibration (the specific heat capacity of the samples was measured using sapphire as reference). The parameters of the temperature-modulated measuring ramp were set to 2 °C/min (heating rate), ± 1 °C (oscillation amplitude) and 60 s (oscillation period) in heat-cool mode. Reading et al.[30] previously showed that these conditions are the best ones for glass transition characterizations on PLA.

High Pressure DSC (HP-DSC) measurements were performed on a DSC 204 HP (Netzsch, Germany) under nitrogen flow (50 mL/min). Prior to measurement, indium, tin, bismuth, lead and zinc standards

were used for energy and temperature calibrations. As previously described, small discs were cut out of the thick PLA film, introduced in pinhole punched aluminum pans and rejuvenated (zero-ageing). The gaseous nitrogen surrounding the sample was then pressurized at different hydrostatic pressures (1, 3, 10, 50, 70, 90 and 100 bar corresponding to 0.1, 0.3, 1, 5, 7, 9 and 10 MPa of hydrostatic compressive stress, respectively). As the pressure stabilized, the samples were heated up at 2 °C/min (coherently with TM-DSC measuring conditions), then cooled down to room temperature at the same rate. The glass transition temperature was measured during cooling.

Results and Discussion

Prior to mechanical compression, rejuvenated PLA 4042D was characterized by running a standard DSC heating ramp; a glass transition temperature $Tg = 58.4 \pm 0.5$ °C was measured as the midpoint of the endothermic step (Figure 1a). The value of ΔCp (heat capacity jump at $T = Tg$) was found to be equal to 0.47 ± 0.07 J/(g · °C) and confirmed that the sample was amorphous, as proved by previous works.[9] The DSC analysis was performed up to 185 °C to prove that the sample is amorphous. Figure 1b shows that after deformation the Tg value increased by a three-degree shift (60.6 ± 0.5 °C). However, by heating again the sample up to 90 °C, a signal identical to the first one was obtained (Figure 1a vs. 1c), which means that the effects of the mechanical compression were entirely recovered. This behavior is similar to what previously observed for other polymers, e.g. polycarbonate.[31]

The values of Tg (midpoint) and ΔCp (Tg) before mechanical deformation, after mechanical deformation and during the second heating ramp are reported in Table 1. Even if small, the three-degree shift observed on the value of Tg is significant. The heat capacity jump at $T = Tg$ gives a hint about the level of disorder of the corresponding amorphous phase. The increased value of $\Delta Cp(Tg)$ after deformation (0.53 J/g°C vs. 0.47 J/g°C) could be explained by the existence of a greater structural disorder. Nevertheless, because of the sample preparation, the error bar on the measured values (± 0.07 J/g°C) is greater than the variations observed. As a consequence, it can be considered that the values of $\Delta Cp(Tg)$ were not significantly modified.

When organic glass-forming liquids are cooled down through their glass transition, the macromolecules got frozen in a spatial configuration whose level of disorder depends, among others, on the cooling rate used to form the glass. Cooling down a glass-forming liquid at higher rates makes it quit the liquid equilibrium curve sooner, i.e. at higher temperatures; an increased cooling

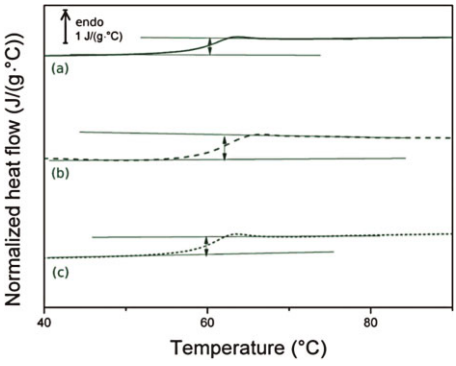

Figure 1.
Standard DSC curves showing the glass transition for rejuvenated PLA 4042D samples before mechanical deformation (a), after mechanical deformation (b) and after heating again the deformed sample up to 90 °C (c). Heating rate = 10 °C/min under nitrogen.

Table 1.
Values of Tg (midpoint) and $\Delta Cp(Tg)$ obtained by standard DSC measurements (Figure 1) for rejuvenated PLA 4042D before mechanical deformation, after mechanical deformation and during the second scan after deformation.

	Tg (°C)	ΔCp (J/(g · °C))
Before deformation	58.4 ± 0.5	0.47 ± 0.07
After deformation	60.6 ± 0.5	0.53 ± 0.07
Second scan after deformation	58.6 ± 0.5	0.46 ± 0.07

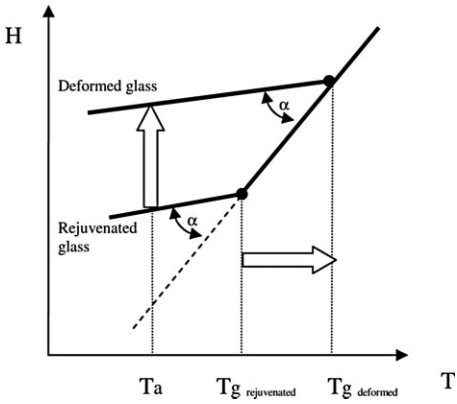

Figure 2.
Sketch exemplifying the effect of a mechanical deformation applied on an amorphous polymer in the glassy state; it could be considered similar to the effect of an increased cooling rate during the formation of the glass.

rate from the liquid produces a glass with a higher level of disorder (the glass out-of-equilibrium curve is higher) and thus a higher glass transition temperature. As exemplified by the sketch in Figure 2, the effect of a mechanical deformation on amorphous polymers in the glassy state is quite similar to what expected when increasing the cooling rate during the formation of the glass. As a consequence, a PLA that would have been previously deformed in the glassy state, when undergoing physical ageing at a given ageing temperature ($Ta < Tg$) will likely need more time to reach the equilibrium state if compared to the same rejuvenated PLA ageing at the same temperature.

TM-DSC is particularly useful to implement Donth's approach,[25] as performing a temperature-modulated heating or cooling ramp to a relaxing glass allows to record a complex thermal response whose real (C') and imaginary (C") components are directly connected to the heat capacity of the sample and to its molecular dynamics respectively. By performing TM-DSC measurements, all the parameters required by equations (1) and (2) can be directly calculated on the C' vs. T and C" vs. T signals. The CRR size of each PLA sample was calculated by exploiting the TM-DSC curves presented in Figure 3; the values of ΔCp were extracted from the C' curves whereas the C" curves, fitted by a Gaussian function, gave the values of T_α and δT required to calculate V_α. The values of T_α, $\Delta Cp(T_\alpha)$ and V_α obtained for these samples are reported in Table 2.

The CRR size of the deformed material (48 ± 5 nm^3) is greater than the one obtained on the initially rejuvenated material (33 ± 3 nm^3); the CRR size obtained during the second scan after deformation

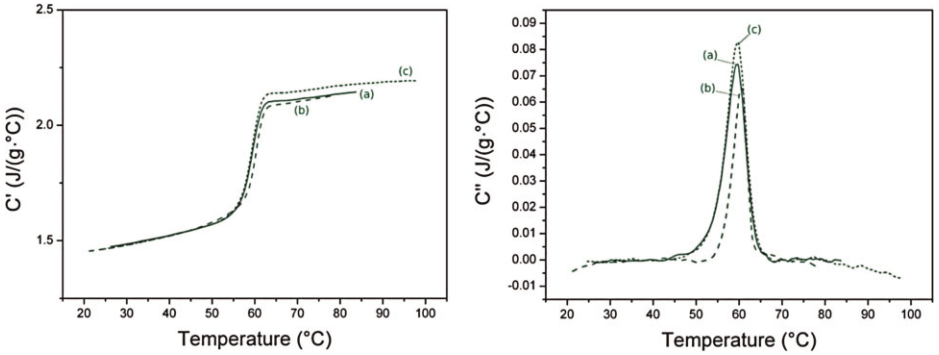

Figure 3.
Real (C') and imaginary (C") components of the complex thermal response obtained by TM-DSC for a sample of PLA 4042D. The same rejuvenated sample was characterized before mechanical deformation (a), after mechanical deformation (b) and after heating it up to 90°C (second scan after deformation) (c). Heating rate = 2 °C/min under nitrogen. Temperature modulation: amplitude ± 1 °C, period 60 s.

Table 2.
Values of T_α and ΔCp (T_α) obtained from the C" vs. T and C' vs. T signals by TM-DSC measurements for a rejuvenated PLA 4042D before mechanical deformation, after mechanical deformation and after an additional rejuvenation (second scan after deformation). V_α values were calculated according to equations (1) and (2).

	T_α (°C)	ΔCp (J/g · °C)	V_α (nm^3)
Before deformation	58.9 ± 0.5	0.48 ± 0.07	33 ± 3
After deformation	60.0 ± 0.5	0.48 ± 0.07	48 ± 5
Second scan after deformation	59.0 ± 0.5	0.53 ± 0.07	25 ± 3

(25 ± 3 nm^3) is even lower. These values suggest that, contrarily to what previously indicated by the values of Tg and ΔCp(Tg), the effects of the mechanical deformation in the glassy state are not entirely reversible when it comes to the molecular dynamics at the glass transition. Moreover, the trend observed for the dependence of the CRR value on the mechanical deformation is not found as expected; if the cooling rate were changed in such a way that the value of the glass transition increases, a decrease of the CRR size would be expected. In this case, the opposite is observed (the mechanical deformation increased both the glass transition temperature and the CRR size).

HP-DSC measurements were not temperature-modulated. When no modulation can be applied to the thermal program (which means that only the normalized heat flow vs. temperature signal is recorded through the glass transition), the values required for equations (1) and (2) cannot be extracted straightaway from the experimental data, as no relaxation peak can be recorded in the absence of a modulation of the temperature. Hempel et al.[32] suggested that a good estimation of the δT value representing the glass transition dynamics can also be obtained by considering the temperature interval ΔT over which the normalized heat flow varies between 16% and 84% of ΔCp(Tg), i.e. the total heat capacity jump at T = Tg (Figure 4).

Figure 5 shows the HP-DSC curves obtained on rejuvenated PLA 4042D. As the measurements were performed during the cooling stage, the glass transition is recorded as an exothermic step. As expected, no relaxation peak related to

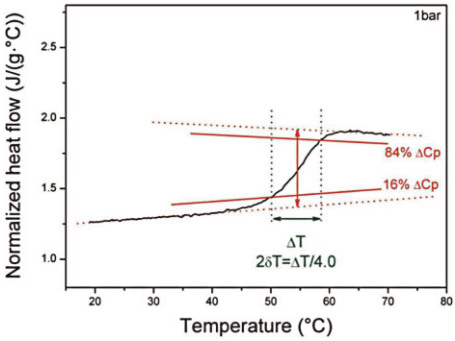

Figure 4.
Normalized heat flow vs. T obtained on rejuvenated PLA 4042D by HP-DSC measurements. Cooling rate = 2 °C/min in the presence of pressurized nitrogen (1 bar). Illustration of the method proposed by Hempel et al.[32] when Donth's model[25] has to be applied on DSC data collected without temperature modulation.

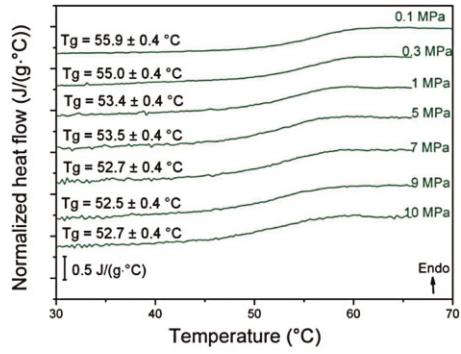

Figure 5.
Thermograms obtained on rejuvenated PLA 4042D by HP-DSC measurements at different levels of hydrostatic pressure (up to 100 bar). The aluminum pans were pierced. Cooling rate = 2 °C/min in the presence of pressurized nitrogen.

physical ageing is observed, which is the only requirement to use Hempel's method[32] to calculate the CRR according to Donth's model.[25]

All the HP-DSC measurements revealed a Tg close to 53 °C (slightly different from the values obtained by standard and TM-DSC because of the different cooling conditions) and not much sensitive to pressure changes. The fact that Tg does not change much with the hydrostatic pressure is not really surprising because it is known, since the works of Lim et al.,[33] that Tg is expected to increase by 35 °C when a pressure of 200 MPa is applied (PVT diagram), whereas the pressure range accessible by the HP-DSC equipment in this work is limited to 13 MPa. HP-DSC measurements made it possible to investigate in more detail a narrower pressure range, which could be the reason why a trend opposite to the PVT diagram of Lim et al.[33] was observed (Tg seems to decrease as the pressure goes from 1 to 10 bar). Whether significant or not, the slight Tg shift observed under pressure is accompanied by a modification of the molecular mobility at the glass transition. Indeed, as shown on Figure 6, a decrease of the CRR size could be detected as pressure increased (18 ± 5 nm^3 at 1 bar vs. 11 ± 3 nm^3 at 10 bar).

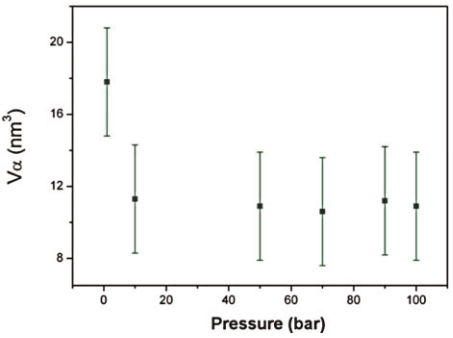

Figure 6.
Pressure dependence of the CRR volume at Tg obtained on rejuvenated PLA 4042D by HP-DSC. Results obtained on thermograms recorded with a cooling rate of 2 °C/min in the presence of pressurized nitrogen at different levels of hydrostatic pressure (1, 10, 50, 70, 90 and 100 bar).

It is worth noticing that the V_α value measured by HP-DSC at 1 bar is almost half the value previously measured by TM-DSC (33 ± 3 nm^3); this must clearly be due to the use of two different methods to extract the parameters needed for Donth's equation (the most accurate method being the one based on TM-DSC measurements). Once again, the values of Tg and ΔCp(Tg) were found to be quite insensitive to small structural constraints, whereas the CRR size allowed to point out even slight modifications of the molecular mobility.

Conclusion

The CRR size of PLA glasses was found to be more sensitive to any variation, however small, of the molecular mobility at the glass transition – even more sensitive than the values itself of Tg and ΔCp(Tg). When the PLA glass was deformed above its limit of elasticity, the CRR size as well as the value of Tg increased, whereas the value of ΔCp(Tg) did not change. Upon heating and successively cooling down a PLA glass that was previously deformed, the values of Tg and ΔCp(Tg) seemed to suggest that the mechanical deformation was entirely reversible; indeed, the CRR size showed that intense mechanical loading in the glassy state should not be considered completely reversible. On the other hand, pressurizing the calorimeter cell during the measurement (up to 100 bar) reduced the CRR size and slightly modified the value of Tg without significantly changing the values of ΔCp(Tg). The conclusion is that Donth's model and the CRR size eventually provide precious complementary information about the glass transition and a better sensitivity to any change in the molecular dynamics of PLA glasses in comparison with the information given by the values of Tg and ΔCp(Tg).

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